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PATENT  
Attorney Docket No. 44492

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

PURUSHOTHAMA RAO

Serial No. 07/852,803

Filed: March 17, 1992

Group Art Unit: 1107

Examiner: M. Nuzzolillo

For: CALCIUM-TIN-SILVER LEAD-  
BASED ALLOYS, AND BAT-  
TERY GRIDS AND LEAD-ACID  
BATTERIES MADE USING  
SUCH ALLOYS

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DECLARATION OF PURUSHOTHAMA RAO

I, Purushothama Rao, do hereby declare as follows:

1. I received a B.S. degree in Physics, Chemistry and Mathematics from the University of Mysore, India, in 1960, a B.E. degree in Metallurgical Engineering from the Indian Institute of Science, Bangalore, India, in 1962, a M.S. degree in Metallurgical Engineering and an M.B.A. from Mankato State University in 1984.

2. I am employed by GNB Incorporated and currently hold the position of Vice President, Research and Development. I have over 19 years experience in the design, development and testing of automotive batteries.

3. I am the inventor of the battery grid and batteries using the calcium-tin-silver-lead alloy described in this patent application. I have reviewed the June 9, 1992 Office Action, as well as translations of Japanese 60-220561 to Nagata and German Patent 27 58 940 to Assmann.

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4. I have also carried out several experiments over a period of time and am continuing to carry out experiments with a variety of batteries using various calcium-tin-silver-lead alloys. Based upon my experience, and in view of the conditions now being faced by automotive batteries in actual service life, it is my belief that it is necessary to evaluate batteries under the standard SAE J240 life test at both 105°F. and also at 167°F. Evaluation of the latter temperature is particularly necessary because of the high under-the-hood temperatures that are now becoming common in many automobiles.

5. In view of the experiments such as those described in the present application, the use of alloys having calcium contents above those used in the present invention but within the range taught by Nagata will not provide the excellent service life characteristics achieved through using the alloys described in the present invention even when the tin and silver contents are in the appropriate range.

6. Further, it has been my experience that, even when an appropriate calcium content is employed, it is also necessary to maintain the tin and silver contents of the alloys employed within the ranges disclosed in the present application if appropriate performance is to be achieved. Thus, I have found that a balance must be provided between the corrosion resistance and the strength requirements for alloys of this type. Use of tin and/or silver contents outside the ranges set forth, but within the ranges taught by Nagata, can, and do, adversely affect the desired performance, often substantially.

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7. Indeed, as is evident from the data set forth in Tables 4 and 5 of the above-identified application, use of the present invention provides at least double the life test performance of previously used alloys when the test regime is carried out at 167°F.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

  
PURUSHOTHAMA RAO

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Declaration of  
Purushothama Rao



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BASED ALLOYS, AND BAT-  
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BATTERIES MADE USING  
SUCH ALLOYS

DECLARATION OF PURUSHOTHAMA RAO

I, Purushothama Rao, do hereby declare and state:

1. I am the named inventor of the above-identified application and have previously submitted a Declaration in this application.

2. I have reviewed the February 24, 1993 Office Action as well as the prior Office Action and the translations of Japanese 60-220561 to Nagata and German Patent 27 58 940 to Assmann. These two reference were cited by the Examiner as pertinent prior art.

3. To provide a satisfactory SLI automotive lead-acid battery used in present-day automobiles, the positive grid alloy used must not only possess superior high temperature positive grid corrosion resistance but must also: (1) possess acceptable mechanical properties in terms of processability and stiffness so that the alloy can be made into battery positive grids under commercial high speed production conditions, and be capable of being subjected to various downstream plate

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processing and eventual battery assembly steps, (2) be capable of allowing the battery to be recharged completely by the automobile's charging system in the event of any inadvertent deep discharge, i.e., leaving the headlights on for a period of several hours when the automobile is parked, and (3) not affect the overall performance and service life of the battery. In other words, the relative high temperature positive grid corrosion resistance properties of a positive grid fabricated from a particular alloy composition becomes immaterial if the alloy cannot be made into grids under production conditions and be capable of being processed under commercial battery manufacturing conditions.

These four important characteristics are very critical in my view and any positive grid alloy chosen must meet all the above four characteristics. Only those alloys that satisfy all the above battery characteristics can be successfully used to manufacture batteries for present-day automobiles and this is true particularly in the present-day automobiles which operate at much higher under-the-hood temperatures and demand the use of maintenance-free-batteries with calcium-tin-lead alloy grid chemistry.

4. In the February 24, 1993 Office Action, the Examiner stated that no evidence had been submitted to show that the present invention provided a lead-acid automobile battery characterized by unexpected results in comparison to the use of the positive grid alloys taught by Nagata and the German patent. In view of the Examiner's statement, I evaluated the

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pertinent performance that would be provided by using positive grid alloy systems containing calcium, tin and silver concentrations outside the levels and ranges set forth in the claims of my patent application but within the concentration ranges set forth in both Nagata and the German patent references cited. Exhibit 1 is a matrix showing the independent and combined effects of each of the three alloying constituents, e.g., calcium, tin and silver in lead matrix on the four critical battery characteristics, which are: (1) mechanical properties and stiffness, (2) high temperature positive grid corrosion resistance, (3) ability to recharge from a deep discharged condition, and (4) overall battery performance and life. As set forth in Exhibit 1, based upon my experience, testing and evaluations, the following conclusions are appropriate and presented herein:

(a) An alloy composition in which the calcium content is below 0.025% by weight possesses such low mechanical properties as to be unacceptable for being able to be manufactured into positive grids using commercially available grid fabricating machines and subsequent plate making and assembly processes used in battery manufacturing. Even heat treating such alloys, as is often used with various alloys, would not result in acceptable mechanical properties. Moreover, the rechargeability of a battery using such an alloy system would be unacceptable, as would be the service life due to a barrier layer that might develop in service and to early failures caused by bent plates from soft grids.

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(b) The use of positive grid alloy compositions having tin below a level of 0.3% by weight would be characterized by poor and unacceptable battery rechargeability characteristics from deep discharge conditions as well as unacceptable overall performance and service life.

(c) Positive grid alloy compositions having tin levels in excess of 0.7 weight percent would have unacceptable service life and overall performance.

(d) Positive grid alloy compositions having silver levels below a level of 0.015% by weight possess only marginal mechanical properties. Even heat treating such alloys, as is often used with various alloys, would not result in acceptable mechanical properties.

For these reasons, the relative high temperature positive grid corrosion resistance characteristics of any of the above-stated positive grid alloy combination systems become immaterial as they do not meet all the four critical positive grid alloy characteristics. Also, from prior testing experience, even if the marginal mechanical properties are ignored, calcium-tin-silver-lead alloys having less than 0.015% silver by weight have unacceptable high temperature positive grid corrosion characteristics.

It also follows, in my opinion, that Nagata and the German patent disclose alloy ranges for calcium, tin and silver that would not provide an acceptable positive grid alloy for a present-day SLI automotive lead-acid battery.



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5. Under my supervision, a series of BCI/SAE Group Size 58-58AmpHr batteries was made and tested to evaluate the high temperature positive grid corrosion resistance of a series of lead-based alloys having calcium, tin and silver contents within the ranges disclosed in either Nagata and/or the German patent that I considered would be a candidate for a positive grid alloy for a present-day SLI automotive lead-acid battery depending upon the high temperature corrosion resistance characteristics of such alloys. High temperature positive grid corrosion resistance was measured as the number of cycles passing in the 167°F SAE J-240 test regimen. These batteries were manufactured under normal production conditions in our Shreveport, Louisiana, manufacturing plant. This series of batteries was made with positive grid alloys containing various levels of calcium, tin and silver. The alloys included in this investigation are listed below:

Alloy Identification	% Calcium	% Tin	% Silver
Claimed Alloy (current production)	0.045	0.5	0.035
800	0.065	0.53	0.001
100	0.068	0.52	0.014
200	0.068	0.67	0.026
500	0.065	0.68	0.040
600	0.064	0.73	0.060
700	0.068	1.42	0.061
400	0.086	0.63	0.039

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While casting these alloys onto battery grids, and as is described in my patent application, aluminum was used in the starting alloy composition as a grid casting processing aid to assist in ensuring that the cast grid would have the desired calcium content. As discussed in my patent application, aluminum present in small quantities in the starting alloy in the range of 0.008 to 0.0180% by weight helps in minimizing the calcium losses in the molten alloy due to oxidation of calcium. Aluminum acts as an oxygen scavenger and ties up all the oxygen present in the molten alloy and eventually accumulates in the drosses and hence very small quantity is left in the finished cast grid. The residual aluminum in the cast grid, if any, would not, in my view, affect the 167°F J-240 life test results or any other battery performance characteristics.

Also, the cast grids made from the alloys having compositions within the claims of my patent application, were heat treated to enhance the initial strength for handling purposes. Again, in my view, this treatment only assists processability and would have essentially no effect on 167°F J-240 life test results.

6. Exhibit 2 sets forth the 167°F SAE J-240 test results of the batteries built with the above various calcium-tin-silver-lead alloy positive grids together with their corresponding positive grid alloy compositions. At present in the industry, the 167°F high temperature J-240 test is used by GNB (and others of which I am aware) as an accelerated laboratory test to simulate actual field service life of the batteries.

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This test duplicates and simulates positive grid corrosion seen in the present-day aerodynamically designed automobiles operating with higher under-the-hood temperatures. There is very good correlation between this 167°F J-240 test results and actual field service in today's automobiles. Unfortunately, two batteries which utilized positive grids formed from alloys within the scope of my claims failed after completing between 3440-4030 J-240 cycles (an average of 3765) due to some mechanical and manufacturing defects. In contrast to all of the other batteries tested which failed due to positive grid corrosion, these batteries with my claimed positive grid alloys, however, failed somewhat prematurely because of the presence of certain manufacturing defects, and the positive grids were still capable of further service life. Accordingly, to provide a service life for the batteries with my claimed alloy positives comparable to what can be achieved in the absence of manufacturing defects, the cycle life results included for the claimed positive grid alloy in Exhibit 2 represents an average of about 20 batteries which were made under normal commercial production conditions.

In addition, to provide a comparison to the previous commercial calcium-tin-lead alloy batteries which is being replaced with the claimed alloy, the average cycle life for that type of battery has likewise been included to provide another benchmark.

As can be seen from Exhibit 2, batteries with all the other positive grid alloy compositions as claimed in the Nagata

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patent and the German patent are yielding anywhere from about 2500 to 3500 high temperature J-240 cycles, while the batteries with the claimed positive calcium-tin-silver-lead alloys are yielding nearly twice as many cycles at about 5600 cycles. The 167°F high temperature J-240 performance of batteries with my claimed calcium-tin-silver-lead positive grid alloy is unmatched by any other lead-calcium-tin or lead-calcium-tin-silver alloys tested, all of which are within the ranges of calcium, tin and silver as set forth in the Nagata and/or German patents. This clearly demonstrates that only my claimed alloys are capable of providing the best high temperature positive grid corrosion resistance while at the same time satisfying the other three critical battery characteristics as stated in Exhibit 1, while alloys claimed in the Nagata and German patents fail to provide batteries with acceptable high temperature positive grid corrosion resistance.

11/22/93 7. Exhibits 3A through <sup>3G</sup>~~3E~~ are photomicrographs of the microstructure of the positive grids made from the alloys shown in Exhibit 2. What can be seen from these photomicrographs is that increasing the silver content to a level of 0.06% by weight results in formation of hot cracks and shrinkage voids in the interdendritic boundaries within the lead matrix as seen in Exhibits <sup>3F and 3G</sup>~~3E~~. The presence of these micro hot cracks as the silver content is increased to 0.06% by weight is independent of either the calcium or the tin content in the alloys. No such micro hot cracks are seen in any of my claimed alloys with a silver content below 0.06% by weight. This propensity to

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develop micro hot cracks as the silver content is increased beyond what is claimed in my application not only adversely affects the processability of grids in the production environment due to their increased susceptibility for brittleness but would also seriously degrade the positive grid corrosion resistance, particularly at high temperatures. In this regard, the German patent teaches the use of silver at 0.06% or higher for the preferred alloy.

8. The microstructures of the various positive grid alloys also reveal that a great deal of microstructure feature similarity exists between the various alloys examined, including my claimed alloys. But yet, the observed high temperature positive grid corrosion resistance as measured by the 167°F J-240 life of all the alloys other than my claimed alloys are nearly the same while only the batteries made with my claimed positive grid alloys exhibit the best high temperature J-240 life.

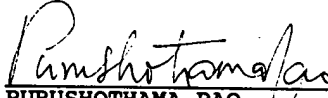
9. Based upon the information provided herein, it is my view that a calcium-tin-silver-lead alloy composition must contain very critical levels of each of the three alloying ingredients as set forth in the claims of my application if the alloy composition is to be acceptable for use as a positive grid alloy in a commercial application for SLI automotive lead-acid battery applications in today's automobiles operating with high under-the-hood temperatures.

10. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on

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information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Further Declarant sayeth not.

  
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PURUSHOTHAMA RAO  
July 22, 93

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